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THERMODYNAMIC AND KINETIC MODELLING OF MICROSTRUCTURE IN A P23/P91 DISSIMILAR WELDMENT

TERMODYNAMICKÉ A KINETICKÉ MODELOVÁNÍ MIKROSTRUKTURY HETEROGENNÍHO SVAROVÉHO SPOJE TYPU P23/P91

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Abstract

Reliability of heterogeneous weldments in power plant applications is determined by their structural stability. Mirostructural evolution in these joints during the long-term thermal/creep exposure is strongly dependent on redistribution of interstitial elements. The "up hill" diffusion of carbon and/or nitrogen across the fusion boundary results in the formation of a decarburized zone on the side of low alloy steel and a carburized zone in high alloy steel. Progress in thermodynamic and kinetic modelling makes it now possible to simulate microstructural changes in heat resistant steels during the long-term service. The reliability of modelling depends strongly on the quality of databases. That is why experimental investigations are required to verify the results of microstructural modelling.

The paper is dealing with the results of thermodynamic and kinetic modelling of microstructural evolution in a P23/P91 heterogeneous weldment during exposure at 500 and 600°C for 30 000 hours. Calculations were carried out using the ThermoCalc and DICTRA software packages. Reliability of calculations was verified by experimental investigations on creep ruptured specimens after exposure at 500, 550 and 600°C for approximately 30 000 hours. Evolution of minor phases in the P23/P91 weld was in a good agreement with results of microstructural modelling, except for the P23 base metal. It has been demonstrated that thermodynamic and kinetic simulations can be used for a realistic prediction of structural stability of heat resistant steels and their joints.

Key words: heterogeneous weldments, "up hill" diffusion

1. Introduction

Integrity of heterogeneous welds during long-term service at elevated temperatures strongly depends on microstructural evolution in individual weld zones [1]. A very important mechanism of microstructural degradation of dissimilar welds represents "up-hill" diffusion of interstitial elements from low alloy steel to high alloy steel [2]. This redistribution of interstitial elements can cause a progressive weakening of low alloy steel close to the fusion boundary. On the other hand the carburized layer on the opposite side of the fusion boundary is much stronger than the surrounding matrix. In nitrogen-bearing steels redistribution of nitrogen is important too.

Progress in thermodynamic and kinetic modelling makes it now possible to simulate microstructural evolution in heat resistant steels and their weld joints during long-term exposure. The semiempirical CALPHAD method is based on the fact that a phase diagram is a representation of the thermodynamic properties of a system. Thus, if the thermodynamic properties are known, it would be possible to calculate the multi-component phase diagrams. Thermodynamic descriptions of lower-order systems (e.g. the Gibbs energy of each phase) are combined to extrapolate higher-order

systems. The reliability of modelling depends strongly on the quality of databases. That is why experimental investigations are required to verify results of microstructural modelling.

In this paper results of thermodynamic and kinetic simulations of microstructural evolution in a P23/P91 heterogeneous weld during long-term exposure at 500 and 600°C are presented. Results of simulations were in some cases verified by experimental investigations.

2. Experimental materials and techniques

The weld joint made of P23 and P91 steel pipes of the dimensions ϕ219x25mm was fabricated in SES Tlmače, Slovakia [3]. A P91 matching filler metal (E CrMo 9 1B, ϕ3.2 and 4.0mm) was applied. The chemical compositions of individual materials in the weldment investigated are stated in Table 1. PWHT was carried out at 750°C for 2hours.

Table 1 Chemical compositions of base materials and the weld metal (WM91), wt. %

Material	C	S	Mn	Si	P	Cu	Ni	Cr	Mo	V	Ti	Nb	W	N	Al
P23	0.08	0.006	0.55	0.27	0.009	0.04	0.08	2.11	0.07	0.23	0.06	0.01	1.70	0.013	0.012
P91	0.11	0.004	0.51	0.38	0.015	0.17	0.42	8.67	1.00	0.23	0.01	0.07	0.01	0.048	0.012
WM91	0.11	0.008	0.66	0.21	0.009	0.04	0.82	9.50	1.02	0.22	0.01	0.04	0.06	0.028	-

An extensive creep rupture testing has been performed on cross weld specimens at temperatures 500, 550 and 600°C in the stress interval from 55 to 200 MPa [4]. Cross weld creep specimens included base materials, heat affected zones and the weld metal. Investigations on minor phases in the creep ruptured specimens after approx. 30 000 hours at 500, 550 and 600°C were carried out on a JEOL JEM 2100 transmission electron microscope equipped with a PGT EDX analyser. Minor phases were identified by both EDX and SAED techniques. Carbon extraction replicas were prepared in following regions of the creep ruptured specimens:

- base materials P23 and P91,
- decarburized zone of the P23 steel,
- carburized zone of the WM91.

Modelling of the thermodynamic equilibrium was carried out using the ThermoCalc software and the STEEL 16 database [5]. Z-phase was not included in this database. Calculations of carbon redistribution and phase profiles across the P23/P91 interface for 500, and 600°C/30 000 hours were performed using the DICTRA software [5]. Modelling did not take into account a concentration profile of solute elements across the fusion boundary. Furthermore the effect of creep strain was not taken into account. Simulation of microstructural evolution included:

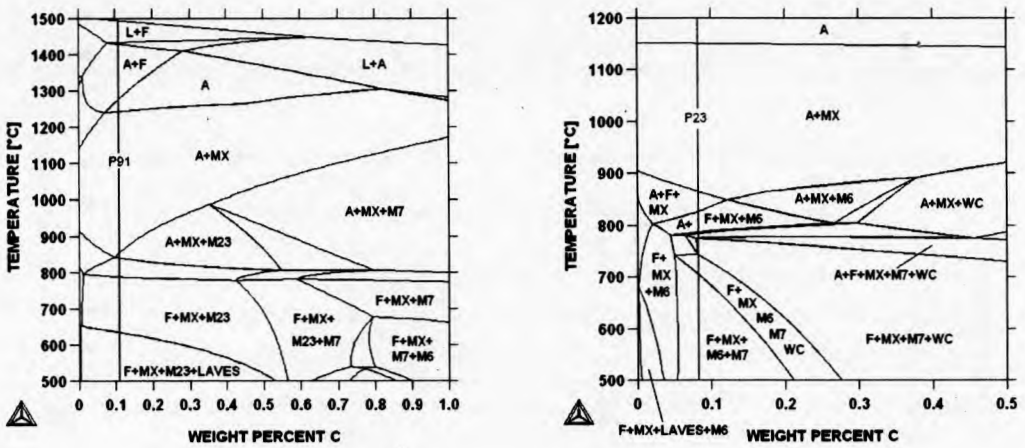
- stable phases in the P23 and P91 steels as a function of temperature and carbon content,
- temperature dependence of carbon and nitrogen activity in the P23 and P91 steels,
- carbon redistribution close to the P23/WM91 boundary,
- phase profiles across the P23/WM91 boundary for temperatures 500 and 600°C and time of exposure of 30 000hours

3. Results of modelling

Thermodynamic modelling

The effects of carbon content on "equilibrium phase diagrams" of P91and P23 steels, as calculated using the ThermoCalc software, are shown in Figs. 1a and 1b, respectively. The blue and red vertical lines represent the carbon content in steels under consideration. As evident an increase of carbon content in the P91 steel decreases Laves phase stability at temperatures of interest, i.e.

between 500 and 600°C. A decline of carbon content in the P23 steel decreases in the temperature interval of interest M_7C_3 stability and at very low carbon contents Laves phase is predicted as the stable minor phase.

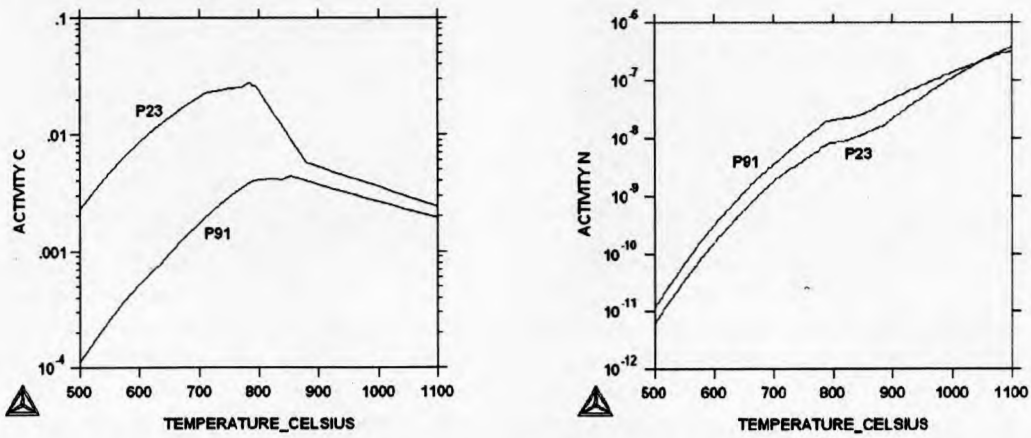


a) b)

Fig. 1 The effect of carbon on "equilibrium phase diagrams of the P91 (a) and P23 (b) steels, where: A=austenite, F=ferrite, M7=M7C3, , M23=M23C6, M6=M6C, LAVES=Laves phase

Kinetic Modelling

Microstructural stability of dissimilar welds is strongly affected by redistribution of interstitial elements in the course of the long-term thermal/creep exposure. Diffusion of interstitial elements is driven by the differences in activities of these elements across the fusion boundary. Atoms move in the direction of activity gradients [6].

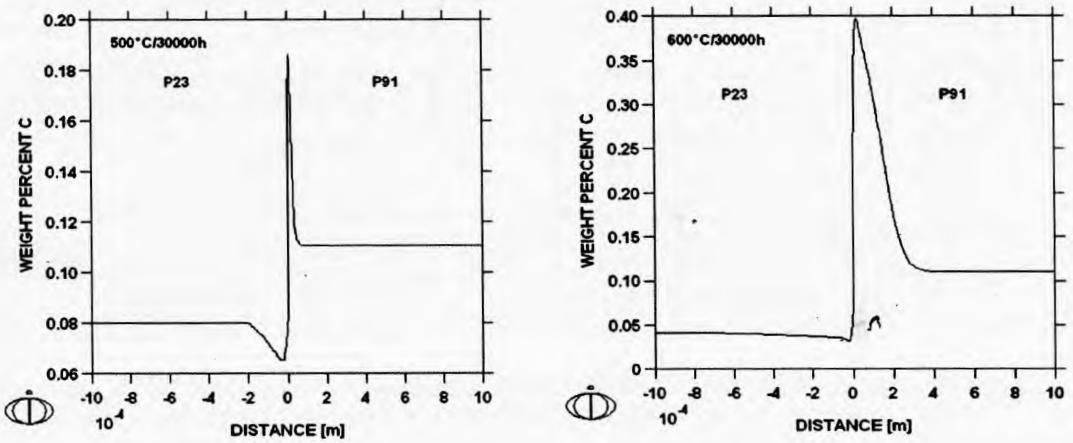


a) b)

Fig. 2 Temperature dependence of carbon activity (a) and nitrogen activity (b) for the P23 and P91 steels

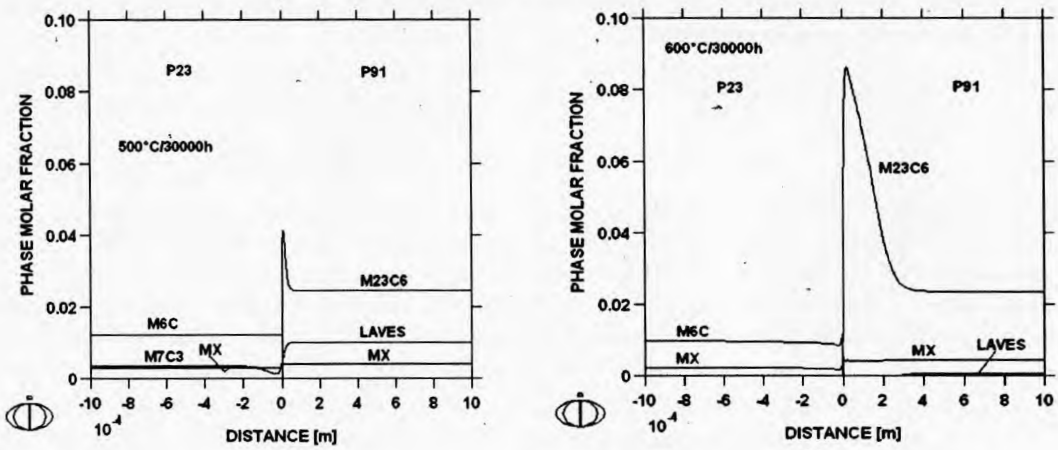
Due to significant differences in carbon activity for the P23 and P91 steels in the temperature range from 500 to 800°C pronounced redistribution of carbon from the P23 to the P91 steel is to be expected, Fig. 2. Above 850°C differences in carbon activity are significantly lower. In the case of nitrogen activity differences are small and that is why no significant redistribution of nitrogen is awaited.

Calculations of carbon migration and phase profiles across the P23/P91 interface for 500°C and 600°C/ 30 000 hours are shown in Figs. 3 and 4, respectively. Results of calculations demonstrate "up-hill" diffusion of carbon from the P23 to the P91 steel. Both the content of carbon and the width of the carburized zone increase with the temperature of exposure. The calculated carburization of the P91 steel for 500°C is 0.18wt%C, while for 600°C it reaches 0.39wt.%C. The predicted partial decarburization of the P23 steel and the width of the partly decarburized zone also increase with the temperature of exposure.



a) b)

Fig. 3 Carbon redistribution across the P23/P91 interface: a) for 500°C/30 000 hours, b) for 600°C/30 000 hours



a) b)

Fig. 4 Minor phase profiles across the P23/P91 interface: a) for 500°C/30 000 hours, b) for 600°C/30 000 hours

The molar fraction of $M_{23}C_6$ phase in the carburized zone increases with the temperature of exposure, but the molar fraction of MX remains about the same and the molar fraction of Laves phase decreases. No other minor phases are expected in the carburized zone. Partial decarburization of the P23 steel takes place mainly at the expense of dissolving M_7C_3 particles. At 600°C no M_7C_3 particles were predicted next to the P23/P91 interface. No significant effect of decarburization on molar fractions of MX and M_6X is predicted.

4. Experimental verification of modelling

Results of experimental studies on minor phases in the individual zones of creep ruptured specimens with time to rupture of approx. 30 000hours are summarised in Tables 2 and 3. The minor phases found in the P91 and WM91 steels are in accordance with the results of ThermoCalc calculations. In the carburized zone of the WM91 a high density of $M_{23}C_6$ particles was present, Fig. 5a. Many fine MX particles were preserved in the partly decarburized zone of the specimen after 26 386 hours at 550°C, Fig. 5b.

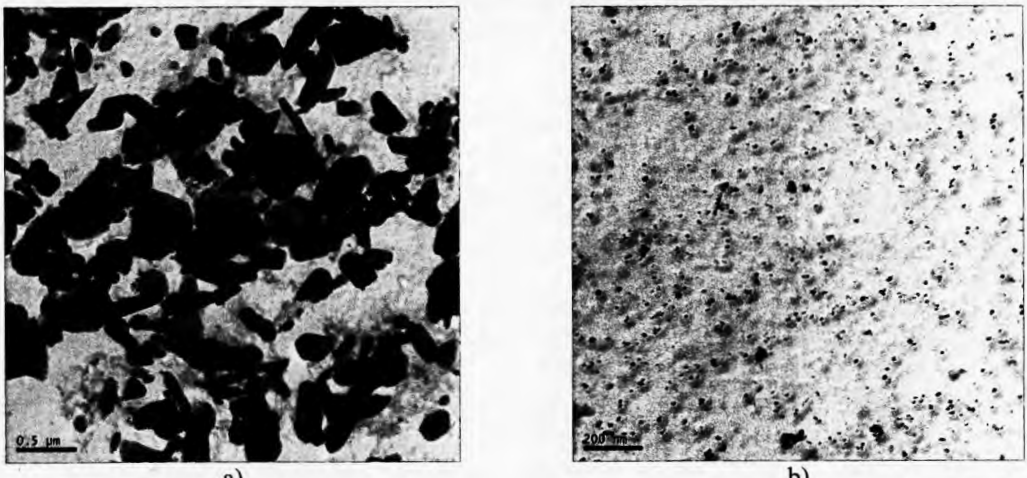
Table 2 Minor phases identified in the specimen after 500°C/31 332 hours

Area	Minor phases
P23	$M_{23}C_6$, M_7C_3, MX
P91	$M_{23}C_6$, NbX, sec. MX, Laves phase

where sec. MX is secondary MX phase (VN)

Table 3 Minor phases identified in the specimen after 600°C/26 780 hours

Area	Minor phases
P23	M_6X, $M_{23}C_6$,MX
P23 decarb. zone	MX,M_6X
WMP91 carb. zone	NbX, $M_{23}C_6$
WMP91	$M_{23}C_6$,NbX, sec. MX, Laves phase
P91	$M_{23}C_6$,NbX, sec. MX, Laves phase



a) b)

Fig. 5 a) Heavy $M_{23}C_6$ precipitation in the carburized zone of the WM91 after creep exposure 600°C/26 780 hours, b) fine undissolved MX particles in the partly decarburized zone of the P23 steel after creep exposure 550°C/26 386 hours

Some differences between calculations and experimental studies were found in minor phases in the P23 steel. During quality heat treatment, precipitation of MX and M7C3 phases was accompanied by precipitation of the M23C6 phase which is regarded as a metastable minor phase in the steel under consideration. Chemical composition of fine MX particles was very variable. Coarser MX particles were rich in titanium and niobium, fine MX particles were rich in vanadium. A significant amount of tungsten was dissolved in MX particles. It has been proved that decarburization of the P23 steel took place at the expense of the M7C3 phase.

M_6C starts to form only during long-term creep exposure. The kinetics of M_6X precipitation depends on both temperature and time of exposure. No M_6X particles were found after exposure 500°C/31 323 hours, but shorter times of exposure at higher temperatures resulted in precipitation of

M_6C particles. After exposure 600°C/26 780 hours many coarse M_6X particles were present in the matrix. These particles were predominantly situated along grain boundaries. In the specimen after 26 780 hours at 600°C a mixture of fine MX and coarser M_6X particles was present in the decarburized zone. The fraction of M_6C particles in this zone was much lower compared with that in the P23 steel unaffected by carbon redistribution [4]. Neither M_6X nor Laves phase particles were found in the carburized zone of the WM91. This is in accordance with simulations. However no M_7C_3 particles were found in the P23 base material after exposure 600°C/26 780 hours, see Table 3. This minor phase has been predicted as a thermodynamically stable phase in the P23 steel.

Fine MX particles preserved in the HAZ of the P23 steel slowed down recovery and recrystallization processes in the bainitic matrix.

5. Conclusions

Thermodynamic and kinetic simulations of microstructural evolution in the P23/P91 heterogeneous weld during long-term exposure at 500 and 600°C have been carried out using the ThermoCalc and DICTRA software packages. Results of calculations demonstrate "up-hill" diffusion of carbon from the P23 to the P91 steel. Only partial decarburization of the P23 steel has been predicted. Both the content of carbon and the width of the carburized zone in the WM91 increase with the temperature of exposure.

Experimental results of minor phase evolution in the P23/P91 weld during long-term exposure at 500 and 600°C are in a good agreement with results of microstructural modelling, except for the P23 base metal. The results prove that thermodynamic and kinetic modeling of microstructural evolution in heat resistant steels is a perspective tool for prediction of structural stability of power plant steels and their joints. The reliability of simulations depends critically on the quality of applied databases.

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